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(54) **Method and sensor for the voltametric determination of oxygen**

(57) The voltametric determination of oxygen dissolved in liquids or present in gaseous mixtures consists in polarization of a sensor by rectangular potential pulses, each pulse being applied after the concentration of oxygen is restored in a space between a separation membrane (3) and the surface of a working electrode (4). The sensor has a limited space (1) filled with electrolyte (6) formed between membrane (3) and working electrode (4), which has advantageously a cylindric shape, the surface area of the base of the space ranges from one third to ten times the surface area of working electrode (4), and the height ranges from 1 to 500 µm.

The limited space (1) may be formed by means of a hole in a foil (2) inserted between membrane (3) and working electrode (4) or it may be formed by a hole in the insulation body (7) of the working electrode (4) between the membrane (3) and the working electrode (4) (Fig. 2).

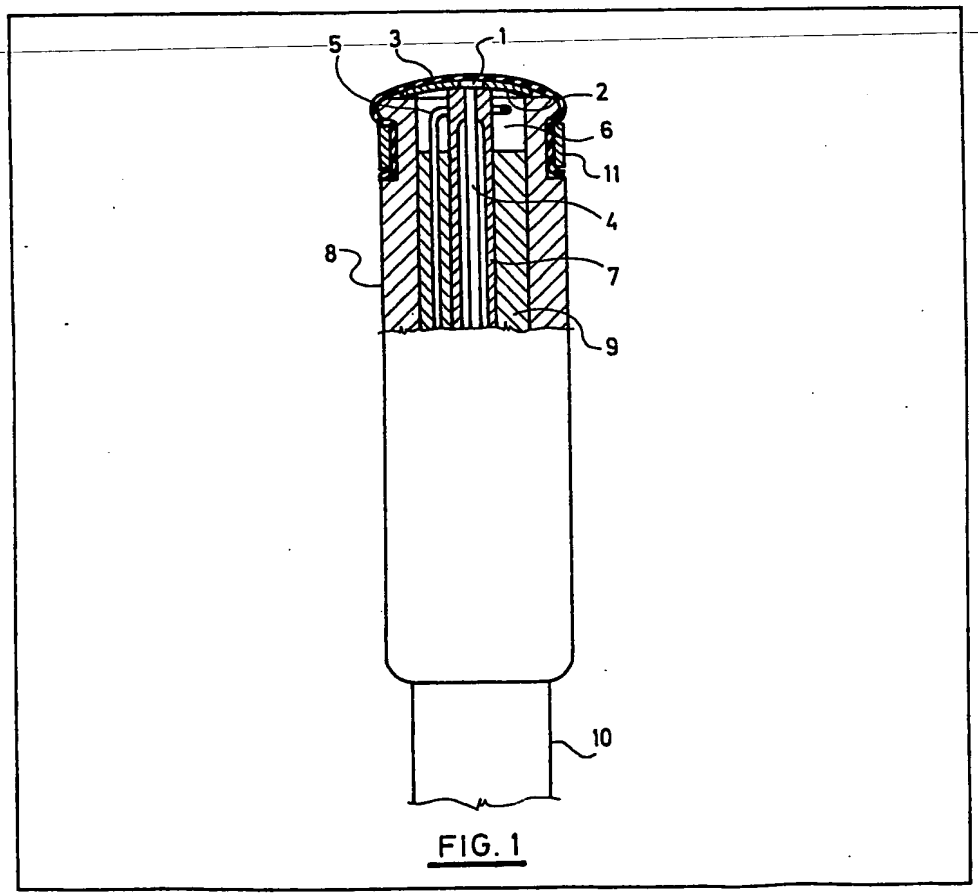

FIG. 1

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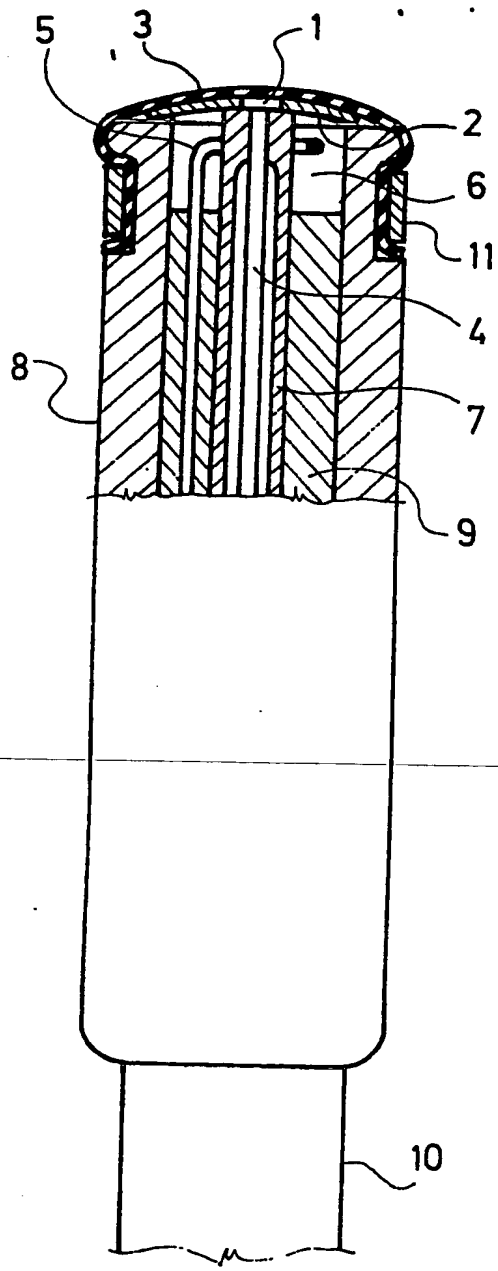

FIG. 1

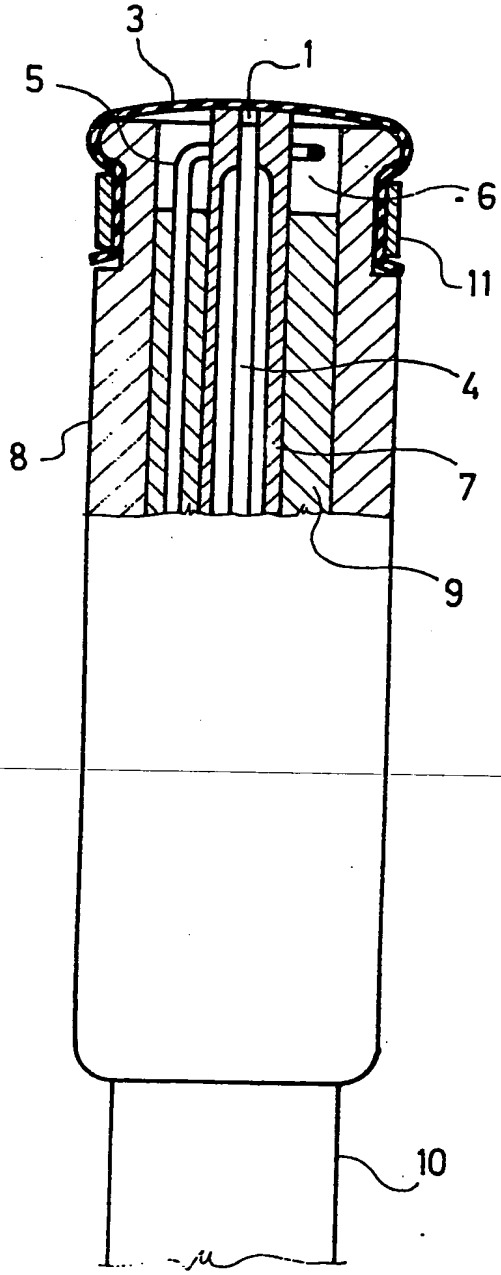

FIG. 2

SPECIFICATION

Method for the voltametric determination of oxygen and a sensor for this method of determination

The invention pertains to a method for the determination of oxygen by an electrochemical voltametric method, on one hand, and to a sensor, which enables this method of determination, on the other hand.

The voltametric or polarographic determination of oxygen has been known for almost 50 years. The first polarographic determination described V. Vítek; Collection Czech. Chem. Commun. *7*, 537-547 (1935). The polarographic determination with a mercury-drop electrode, which was separated from the measured solution with a permeable membrane, was described by one of the authors of this invention, viz. L. Šerák; Z. Phys. Chem., Leipzig, Sonderheft, 1958, p. 84. The determination with a solid working electrode separated from the sample by a layer of electrolyte was described by P. W. Davies and F. Brink; Rev. Sci. Instrum. *13*, 524, 1942, while the determination with a solid working electrode separated from the measured sample with a membrane was described by L. C. Clark; Trans. Amer. Soc. Art. Int. Organs *2*, 41-45 (1956).

In the papers mentioned above, the voltametric determination of oxygen was gradually improved and, at the present time, it is carried out by a procedure based on the work of L. C. Clark; see e.g. H.P. Kimich, F. Kreuzer, J. G. Spaan; Biocapt *75*, 307-312 (1975). In the arrangement of Clark, a sensor consists of a working polarized solid electrode, a reference electrode, an electrolyte and a membrane, which is permeable for oxygen and impermeable for water, ions and large molecules, so that only a thin layer of electrolyte occurs between the membrane and the surface of working electrode. The working electrode is cathodically polarized to a constant potential and, at constant temperature, the current passing through the sensor is directly proportional to the amount of oxygen transported to the surface of working electrode and, consequently, to the oxygen concentration in the investigated medium in a close proximity of the membrane. However, excellent properties of the sensor are accompanied with an unfavourable feature, namely with a pronounced dependence of the current signal on temperature (the signal increases as much as by 8% at the temperature increase of 1°C). This dependence is predominantly determined by a high temperature coefficient of the membrane permeability to oxygen. The permeability increases exponentially with the increasing temperature. In practical measurements, the temperature dependence of signal has to be compensated automatically, which fact limits the reproducibility and correctness of measurement at larger temperature differences.

The above mentioned disadvantage is removed by the present method of pulse voltametric determination and the sensor according to the invention, which is based on a periodic polarization of the sensor by rectangular potential pulses, whereas each pulse follows first after the concentration of oxygen, in a limited space filled with electrolyte and formed between the membrane and the surface of working electrode, is restored.

A choice of the length of interval between individual pulses, ranging from 1 to 10 s or more, depends on properties of the membrane and on dimensions of the limited space.

The invention further pertains to the sensor for performing the method according to the invention, wherein a limited space filled with electrolyte is formed between the membrane and the working electrode, which space has advantageously a cylindric form, has a surface area of its base ranging from one third to ten times the surface area of the working electrode, and its height ranges from 1 to 500 µm.

This limited space may be created by means of a hole in a foil, which is inserted between the membrane and the working electrode. The limited space can be also formed by a hole in an insulation body of the working electrode between the membrane and the working electrode. It is suitable, if the hole in the insulation body or working electrode is placed in the longitudinal axis of the working electrode.

An information about oxygen concentration is obtained by measuring an instant current in a precisely set moment after the beginning of pulse, when a charging current of double-layer has already quenched and the concentration gradient of oxygen is confined in the limited space between the membrane and the surface of working electrode.

The appended drawings display two examples of the sensor according to the invention in a longitudinal cross-section; Fig. 1 shows the sensor, the limited space of which is created by means of a hole in a foil inserted between the membrane and the working electrode, whereas Fig. 2 shows the sensor with the limited space formed by a hole in the insulation body of working electrode between the membrane and the working electrode.

The sensor consists of a jacket of sensor *8* separated by a layer of cement *9* from a reference electrode *5* and also from an insulation body *7* of working electrode, which guides the working electrode *4* in the longitudinal axis of the sensor. Both electrodes are connected by one end to a coaxial cable *10*, whereas their other ends project into the space of electrolyte *6*. The electrolyte *6* is separated from environment by means of a membrane *3*, which is fixed to the sensor jacket *8* by means of an fixation ring *11*. In the first example of the sensor according to the invention (fig. 1), a foil *2* with a cylindric hole is inserted between the membrane *3* and the jacket *8* of sensor in the space of electrolyte *6*, which creates a limited space *1* between the working electrode *4* and the membrane *3*, whereas in the second example of the sensor (Fig. 2), the limited space *1* is formed by a hole in the insulation body *7* of the working electrode *4* between the membrane *3* and the working electrode *4*.

Measurement of the instant current in a precisely set moment after the beginning of pulse, when the charging current of double-layer has already quenched and the concentration gradient of oxygen is

confined in the limited space *1* between the membrane *3* and the surface of working electrode *4*, gives data which serve for the determination of oxygen concentration.

The invention may be employed at technological conditions for the determination of oxygen either dissolved in liquids or present in gaseous mixtures.

CLAIMS

1. A method for the voltametric determination of oxygen by means of a sensor, comprising a separation membrane and a working electrode, and an evaluation device of the signal, wherein the sensor is polarized by rectangular potential pulses, whereas each pulse follows first after the oxygen concentration is restored in a space between the separation membrane and the surface of working electrode.

2. A sensor for performing the method according to Claim 1, comprising a working electrode, an insulation body of working electrode, a nonpolarizable reference electrode, an electrolyte, and a separation membrane, wherein a limited space (1) filled with the electrolyte is created between the membrane (3) and the working electrode (4), which base has a surface area ranging from one third to ten times the surface area of the working electrode and which height ranges from 1 to 500 μm.

3. A sensor according to Claim 2, wherein the limited space (1) is formed by a hole in a foil (2), which is inserted between the membrane (3) and the working lectrode (4).

4. A sensor according to Claim 2, wherein the limited space (1) is formed by a hole in the insulation body (7) or working electrode (4) between the membrane (3) and the working electrode (4).

5. A sensor according to Claim 4, wherein a hole in the insulation body (7) of the working electrode (4) is placed in the longitudinal axis of working electrode (4).

6. A sensor according to Claims 2 through 5, wherein the limited space (1) has a cylindric shape.

7. A method for the voltametric determination of oxygen by means of a sensor substantially as described and disclosed herein.

8. A sensor for performing the method for the voltametric determination of oxygen by means of a sensor substantially as herein described with reference to Figure 1 or Figure 2 of the accompanying drawings.

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